

The Preparation of Copper(I) Complex Containing Organic Halide*¹

Keisuke WADA and Harukichi HASHIMOTO

Department of Synthetic Chemistry, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo

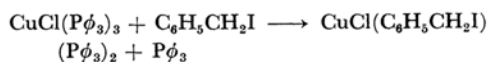
(Received June 14, 1968)

The copper ion catalysed reactions of organic halides have been extensively studied for their potent utilities in the field of organic synthetic chemistry. One important subject still remaining is the elucidation of the nature of the interaction between organic halide and copper ion. An approach to this problem is the preparation of a relatively stable complex of intermediate character of the reaction between organic halide and copper ion. Organocopper compound that involves copper-carbon bond is a fairly familiar one.¹⁾ Only a little is known, however, about a compound that involves the direct interaction between copper and halogen atom in the organic halide. In 1914, Peters prepared the cuprous cyanide complex coordinated by methyl iodide.²⁾ Since then no remarkable study has been reported on this type of the compound.

During the course of studies on the redox ligand transfer reaction or organic halide with transition metal complex,³⁾ we discovered new complexes of general formula $\text{CuX}(\text{organic halide})(\text{P}\phi_3)_2$. The complexes were obtained by the reaction of cuprous chloride, triphenylphosphine and organic halide in acetonitrile solutions under a nitrogen

stream at reflux. The complexes were separated from reaction mixture as precipitates and after repeated washing with ethyl ether, were dried *in vacuo*. Typical of these complexes is that of benzyl iodide.

The same complex was obtained also by the reaction of tris(triphenylphosphine)-copper(I) chloride and benzyl iodide. The yield was nearly stoichiometric in this case.



Found: C, 61.98; H, 4.23; Cu, 7.52%. Calcd for $\text{CuCl}(\text{C}_6\text{H}_5\text{CH}_2\text{I})(\text{P}\phi_3)_2$: C, 61.36; H, 4.43; Cu, 7.55%. The complex is white crystalline and rather sensitive to light but fairly stable against oxygen. The infrared spectrum of the complex gives a sharp strong band at 581 cm^{-1} and several other bands due to triphenylphosphine and benzyl iodide. The 581 cm^{-1} band is assigned to C-I stretching of benzyl iodide coordinated to copper atom, although there remains some uncertainty. The NMR spectrum of methylene proton at elevated temperature gives a signal at 5.08 ppm. The signal of free benzyl iodide at the same condition appears at 5.33 ppm. The ultraviolet spectrum shows a new band at $250\text{ m}\mu$.

The reaction of this complex and ethylenediamine in acetonitrile produces a trace of bibenzyl. The complex of this type may be the precursor of intermediate in the redox ligand transfer reaction of organic halide.³⁾

*¹ Oxidation-Reduction Reactions by Transition Metal Complexes. IV.

1) H. Hashimoto and T. Nakano, *J. Org. Chem.*, **31**, 891 (1966).

2) W. Peters, *Z. Anorg. Allgem. Chem.*, **89**, 191 (1914).

3) K. Wada and H. Hashimoto, *This Bulletin*, **41**, 3001 (1968).